

# REDUCTION OF NO WITH NH<sub>3</sub> ON TiO<sub>2</sub>-, Al<sub>2</sub>O<sub>3</sub>- AND Fe<sub>2</sub>O<sub>3</sub>-SUPPORTED METAL OXIDE CATALYSTS

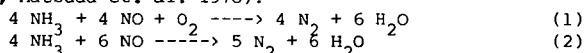
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## INTRODUCTION

The pollution of the atmosphere by nitrogen oxides (NO<sub>x</sub>=NO+NO<sub>2</sub>) has been a subject of growing concern during the past decade. During combustion, NO<sub>x</sub> is formed either by reaction of oxygen and atmospheric nitrogen (thermal NO<sub>x</sub>) or conversion of chemically bound nitrogen in the fuel (fuel-NO<sub>x</sub>). The major fraction of these emissions results from the fuel-NO<sub>x</sub> during combustion in industrial and utility boilers. The formation of NO<sub>x</sub> in the boilers can be reduced to a considerable extent by modification in the combustion technique, for example by applying fluidized bed combustion boilers. There still will remain some NO<sub>x</sub> in the flue gases. Hence, other additional methods have been introduced for NO<sub>x</sub>-removal.

The most widely applied method for decreasing NO<sub>x</sub> emissions from existing stationary sources is selective catalytic reduction (SCR) by NH<sub>3</sub>. The most commonly proposed overall reactions between NO and NH<sub>3</sub> are (Odénbrand et al. 1985, Matsuda et al. 1978):



The catalyst used in a commercial plant must possess high activity and selectivity, since the volume of flue gas to be treated is large. In addition, the catalyst must be resistant to SO<sub>2</sub> poisoning (Matsuda et al. 1982, Nam et al. 1986). The purpose of the present study was to examine the kinetics of NO-NH<sub>3</sub>-O<sub>2</sub> reactions on several catalysts promoting the SCR of NO<sub>x</sub>.

## EXPERIMENTAL

### Catalysts.

The catalysts and their main characteristics are shown in Table 1. The catalysts were supported base metal oxides. Some other materials were also tested for their catalytic activity.

Table 1. Catalysts in experiments.

Catalyst	Pellet size(mm)	Specific surface area(m <sup>2</sup> /g)	Bulk density(g/ml)
1. V(4%)/TiO <sub>2</sub>	>2.0	7	1.1
2. Cu(5%)/TiO <sub>2</sub>	>2.0	7	1.0
3. Fe(6%)/TiO <sub>2</sub>	>2.0	14	1.1
4. Ni(5%)/TiO <sub>2</sub>	>2.0	6	0.8
5. Cu(7%)/Al <sub>2</sub> O <sub>3</sub>	3.2	140	1.0
6. Cr(14%)/Al <sub>2</sub> O <sub>3</sub>	4.0	60	1.1
7. Ni(11%)/Al <sub>2</sub> O <sub>3</sub> (Ni P)	3.2	80	1.1
8. Ni(16%)/Al <sub>2</sub> O <sub>3</sub> (Ni T)	2.0-4.0	210	0.8
9. Slag A (13% Fe)	>1.0	1.4	1.6
10. Slag B (0.4% Fe)	>1.0	0.2	1.1
11. Hematite (66% Fe)	0.2-1.0	<0.1	3.1
12. Ilmenite (36% Fe)	>2.0	0.6	1.1
13. Ilmenite+TiO <sub>2</sub> (5% Fe)	>2.0	-	1.0

The  $\text{TiO}_2$ -based catalysts were prepared according to methods developed by Matsuda et al. (1982), Saleh et al. (1986) and Skvortsov et al. (1977).  $\text{TiO}_2$  (anatase) was wet-impregnated in a solution of a salt of the active material (V, Cu, Fe, Ni). After drying for 24 hours at  $110^\circ\text{C}$  the catalyst was calcined in air at  $400^\circ\text{C}$ . The  $\text{Al}_2\text{O}_3$ -supported catalysts were commercially available materials. The other materials in the experiments were inexpensive iron-containing slags and ores.

The total specific surface areas of the fresh materials were obtained with a Perkin-Elmer 212 C Sorptometer.

#### Apparatus and reactant gases

The schematic diagram of the experimental apparatus is presented in Figure 1. The fixed bed reactor and a pre-heater were made of quartz. The reactor was heated in a Heraeus ROK 4/60 oven and the temperature in the catalyst bed was measured with a Ni-NiCr-thermocouple. The gases were supplied from pressure bottles via high precision Hi-Tech massflowmeters. Gas lines before the pre-heater were made of stainless steel. The mixing of  $\text{NH}_3$  with the simulated flue gas took place after the pre-heater, just in front of the reactor, in order to avoid any homogeneous reactions between the components.

Two teflon sampling lines were connected to the reactor. The gas mixture was transported through a EPM 797 diluting unit to a Monitor Labs 8840 chemiluminescent  $\text{NO}_x$ -analyser. The analyser was equipped with a thermodynamic converter (Monitor Labs 8750) and it measured  $\text{NO}_x$  and  $\text{NO} + \text{NH}_3$ .  $\text{NH}_3$  was calculated by difference. The equipment was calibrated with a gas having 200 ppm  $\text{NO}$ .

#### Procedures

The  $\text{NO}-\text{NH}_3-\text{O}_2$  reaction was studied in both an empty tubular reactor and a packed bed reactor with different catalysts. After the temperatures of flue gas in the catalyst bed reached the set value, the concentration of  $\text{NO}_x$  was measured until a steady-state reading was obtained. The experimental operating conditions are summarized in Table 2.

Table 2. Experimental operating conditions.

Inlet	$\text{NO}$	0-2000 ppm
concentration	$\text{NH}_3$	0-2000 ppm
	$\text{O}_2$	0-5 %
	$\text{CO}_2$	0 or 10 %
	$\text{SO}_2$	0 or 500 ppm
	$\text{N}_2$	carrier gas
Volumetric flow rate		$0.57-0.64 \text{ m}^3(\text{NTP})/\text{h}$
Catalyst bed volume		50 $\text{cm}^3$
Space velocity (SV)		$3.2-3.6 \text{ m}^3 \text{ flue gas}(\text{NTP})/\text{m}^3(\text{cat})\text{s}$
Temperature		$200-900^\circ\text{C}$
Duration of the test		0.25 - 6 h

The  $\text{SO}_2$  poisoning experiments were performed with a test gas containing 500 ppm  $\text{SO}_2$  using the  $\text{Cu}/\text{Al}_2\text{O}_3$ ,  $\text{Cr}/\text{Al}_2\text{O}_3$ ,  $\text{Cu}/\text{TiO}_2$  and  $\text{V}/\text{TiO}_2$  catalysts.

### **RESULTS AND DISCUSSION**

#### Empty reactor

Figure 2 shows the plot of  $\text{NO}_x$  conversion versus temperature from 300 to  $900^\circ\text{C}$ . The empty reactor had negligible effects on the  $\text{NO}$  decomposition. The small effect of the quartz tube on the reaction between  $\text{NO}$  and  $\text{NH}_3$  was also small. The thermal reduction of  $\text{NO}$  by  $\text{NH}_3$  increased once the temperature reached  $900^\circ\text{C}$ . At this temperature the  $\text{NO}$  conversion was 26 %.

#### TiO<sub>2</sub>-supported catalysts

The concentrations of NO<sub>x</sub> after a one hour operation with the Cu, V, Ni and Fe catalysts are shown in Figure 6 as a function of the catalyst temperature. The conversion of NO increased rapidly until about 300 °C which seemed to be the optimal temperature for all these catalysts. Above this temperature the NO<sub>x</sub> concentrations increased. This was due either to the incomplete reduction of NO with NH<sub>3</sub> or direct oxidation of NH<sub>3</sub> with the excess oxygen present or a combination of both factors.

The V/TiO<sub>2</sub> catalyst showed high activity and resistance to SO<sub>2</sub> poisoning (Figure 7). The Cu catalyst lost its activity under 350 °C in the presence of SO<sub>2</sub> (Figure 8). Sulfur was not found to accumulate in great degree on this catalyst at 350 °C (Fresh: 0.23 % S; After SO<sub>2</sub>-test: 0.40 % S). The Fe and Ni catalysts were less active than the V and Cu catalysts. Wong et al. (1986) have shown that the activity of TiO<sub>2</sub>-based iron oxide catalysts is strongly affected by the preparation procedure.

#### Al<sub>2</sub>O<sub>3</sub>-supported catalysts

Four commercial Al<sub>2</sub>O<sub>3</sub>-supported catalysts were investigated. These catalysts had large specific surface areas (between 60 and 140 m<sup>2</sup>/g). The results with these catalysts are shown in Figure 3. The optimal operation temperatures were between 300 and 350 °C in the absence of SO<sub>2</sub>. The highest measured conversions were 80 (Cu), 74 (Ni P), 56 (Cr) and 40 % (Ni T) after a one hour operation.

The activity of the Cu catalyst improved in the presence of SO<sub>2</sub> at temperatures above 350 °C (Figure 4). Nam et al. 1986 have found with a V/Al<sub>2</sub>O<sub>3</sub> catalyst similar results. They proposed that the sulfur contamination as, Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, increased the NO conversion at temperatures above 400 °C, presumably due to the moderation of the competing reaction of the NH<sub>3</sub> oxidation to NO. Another reason for the behavior can be the formation of CuSO<sub>4</sub>, which is also known to catalyze the reaction concerned (Schrod 1986). Sulfur was accumulated on our Cu/Al<sub>2</sub>O<sub>3</sub> catalyst at 350 °C (Fresh: 0.02 % S; After SO<sub>2</sub>-test: 3.32 % S). Compared with the results with TiO<sub>2</sub>-supported catalysts, it can be concluded that the formation of Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> is probable on Al<sub>2</sub>O<sub>3</sub>-supported catalysts.

The activity of the Cr catalyst decreased at temperatures under 350 °C when SO<sub>2</sub> was present (Figure 5). The life of this catalyst seemed to be short under these circumstances. According to Ando (1983) a portion of SO<sub>2</sub> oxidizes to SO<sub>3</sub> on the catalyst surface to form NH<sub>4</sub>HSO<sub>4</sub>. The SO<sub>2</sub> poisoning test time was too short to make any accurate conclusions about the effects of SO<sub>2</sub>.

It could be concluded that NO reacts with NH<sub>3</sub> at a 1:1 mole ratio at the optimal operation temperature as proposed by Kato et al. (1981). The NH<sub>3</sub> concentration decreased in a similar way than the NO<sub>x</sub> concentration until about 350 °C. Above that temperature the concentration stayed under 100 ppm. The degree of NH<sub>3</sub> oxidation by O<sub>2</sub> increased when the temperature rose over 350 °C.

#### Other materials tested.

Iron oxide containing materials vary widely in catalytic activity depending on the composition (Moriguchi et al. 1978). The results of our tests are shown in Figure 9.

At low temperatures (200 - 350 °C) reaction kinetics has a decisive role. In the case that the catalytic material is poorly distributed or the available surface is low, no discernible reaction is observed. When the temperature is increased all reactions, e.g. also the NH<sub>3</sub> oxidation reaction, are speeded up and the final result in a NH<sub>3</sub>-NO-O<sub>2</sub>-system may be either a balance between the competing reactions or, in the worst case, an increase of NO<sub>x</sub> from NH<sub>3</sub> oxidation. The above explanations apply to some of the slag catalysts. The specific surface areas of the investigated materials were probably not sufficient for a measurable selective catalytic reduction.

For the  $\text{NO-NH}_3\text{-O}_2$  reaction the investigated materials can be divided in four groups:

- A. Good catalysts ( $\text{V/TiO}_2$ ,  $\text{Cu/TiO}_2$ ,  $\text{Cu/Al}_2\text{O}_3$  and  $\text{Cr/Al}_2\text{O}_3$ )
- B. Inferior catalysts ( $\text{Ni T/Al}_2\text{O}_3$ )
- C.  $\text{NH}_3$  oxidation catalysts ( $\text{Fe/TiO}_2$ ,  $\text{Ni/TiO}_2$ , slag A and iron containing ores)
- D. Noncatalytic materials (Slag B)

Good catalysts are predicted to be promoting both competitive reactions: NO reduction and straight  $\text{NH}_3$  oxidation.

#### Influence of oxygen.

The role of oxygen in SCR becomes greater when the  $\text{O}_2$  concentration falls below 1 % (Figure 10, 11 and 12). The oxygen affects the reaction rate of NO with  $\text{NH}_3$  as found also by Matsuda and Kato (1983). An  $\text{O}_2$  concentration of 0.1 % was near to the critical value for the NO conversion with the  $\text{Cu/Al}_2\text{O}_3$  catalyst (Figure 10). Kotter et al. (1986) have also shown that an  $\text{O}_2$  concentration below 0.2 % changes the reaction rate markedly.

The NO reduction using the  $\text{Cu/Al}_2\text{O}_3$  catalyst has an optimal operation temperature at about 300 to 350 °C in the presence of 1 to 5 %  $\text{O}_2$ . In the absence of oxygen the NO reduction proceeds according to the reaction (2) at higher temperatures (>350 °C). There exists no oxidation of  $\text{NH}_3$  to NO and the higher temperatures favour this reaction kinetically.

The absence of  $\text{O}_2$  inhibits the NO reduction on  $\text{TiO}_2$ -supported catalysts at 300 to 350 °C. Oxygen concentrations between 1 to 5 % were shown to have some influence only at temperatures below 300 °C especially with  $\text{V/TiO}_2$  catalyst. The possibilities of the formation of  $\text{N}_2\text{O}$  become greater when oxygen is absent (Otto and Shelef 1972).

#### The influence of inlet NO concentration.

The conversions with  $\text{Cu/Al}_2\text{O}_3$  catalyst at different inlet NO concentrations are shown in Figure 12. The degree of NO reduction increases with NO inlet concentration. It is easier to reach the low outlet concentration if the inlet concentration is as low as possible. When the reactant concentration (NO and  $\text{NH}_3$ ) falls below 100 ppm the reaction rate of SCR, however, decreases sharply.

### CONCLUSIONS

Thirteen different SCR catalysts were investigated at temperatures between 200 to 900 °C. Oxygen affects the reaction rate of NO with  $\text{NH}_3$ . In the presence of  $\text{O}_2$  the NO reduction has an optimum temperature between about 300 to 400 °C. In the absence of  $\text{O}_2$  the NO reduction is shifted to higher temperatures. The  $\text{V/TiO}_2$  catalyst is resistant to  $\text{SO}_2$ . The activities of the other catalysts investigated are affected by  $\text{SO}_2$ . There is a clear difference between the  $\text{Al}_2\text{O}_3$ - and  $\text{TiO}_2$ -supported catalysts in regard to the influence of  $\text{SO}_2$ .

### ACKNOWLEDGMENTS

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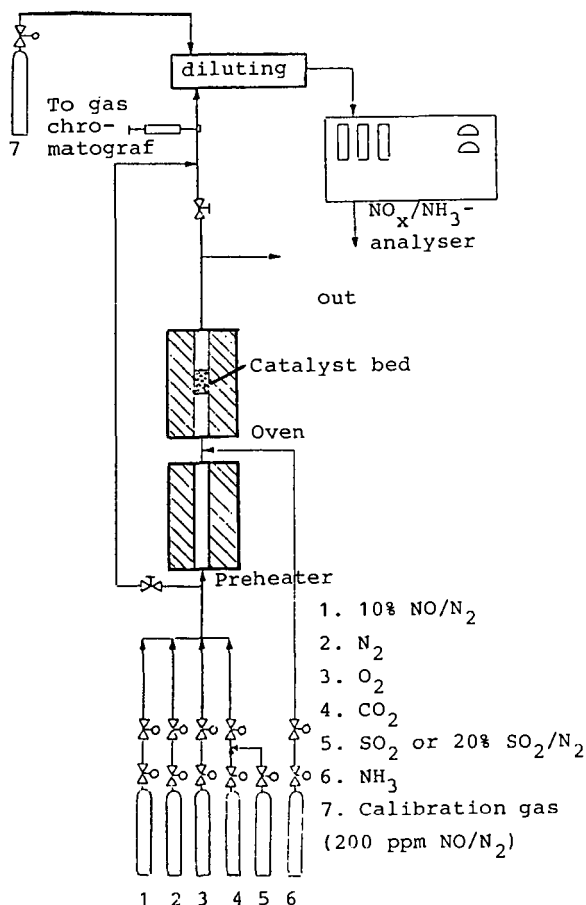


Figure 1. A schematic diagram of the experimental apparatus.

Figure 2. Thermal NO conversion in the quartz tube ( $\text{NO} = 500 \text{ ppm}$ ,  $\text{O}_2 = 5 \%$ ,  $\text{SV} = 3.6 \text{ s}^{-1}$ ,  $\text{SO}_2 = 0$ ).

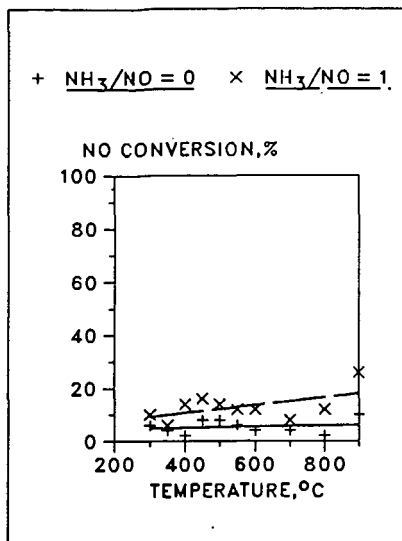


Figure 3. NO conversion with the  $\text{TiO}_2$ -supported catalysts ( $\text{NO} = 500 \text{ ppm}$ ,  $\text{NH}_3/\text{NO} = 1$ ,  $\text{SV} = 3.6 \text{ s}^{-1}$ ,  $\text{SO}_2 = 0$ ).

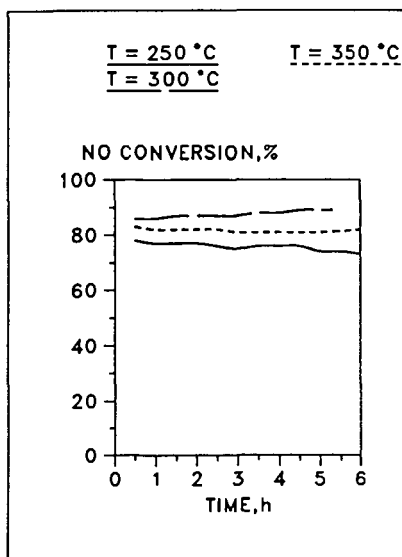
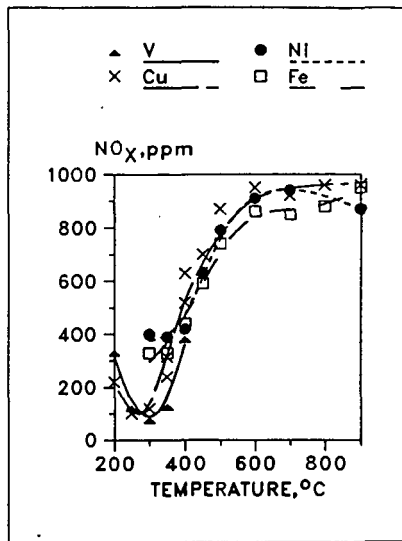


Figure 4. The influence of  $\text{SO}_2$  on the NO conversion with the  $\text{V}/\text{TiO}_2$  catalyst ( $\text{NO} = 500 \text{ ppm}$ ,  $\text{NH}_3/\text{NO} = 1$ ,  $\text{SV} = 3.2 \text{ s}^{-1}$ ,  $\text{SO}_2 = 500 \text{ ppm}$ ).

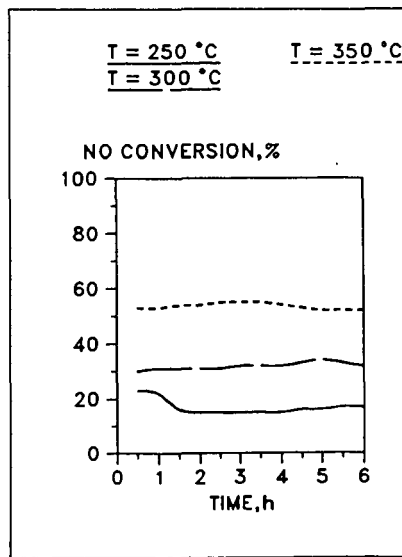


Figure 5. The influence of  $\text{SO}_2$  on the NO conversion with the  $\text{Cu}/\text{TiO}_2$  catalyst ( $\text{NO} = 500 \text{ ppm}$ ,  $\text{NH}_3/\text{NO} = 1$ ,  $\text{SV} = 3.2 \text{ s}^{-1}$ ,  $\text{SO}_2 = 500 \text{ ppm}$ ).

Figure 6. NO conversion with the  $\text{Al}_2\text{O}_3$ -supported catalysts ( $\text{NO}=500$  ppm,  $\text{NH}_3/\text{NO}=1$ ,  $\text{SV}=3.6 \text{ s}^{-1}$ ,  $\text{SO}_2=0$ ).

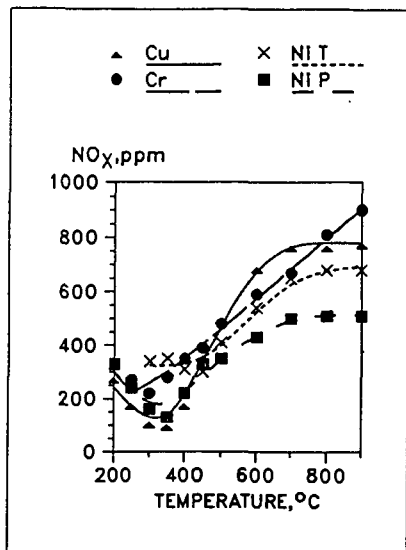


Figure 7. The influence of  $\text{SO}_2$  on the NO conversion with the  $\text{Cu}/\text{Al}_2\text{O}_3$  catalyst ( $\text{NO}=500$  ppm,  $\text{NH}_3/\text{NO}=1$ ,  $\text{SV}=3.2 \text{ s}^{-1}$ ,  $\text{SO}_2=500$  ppm).

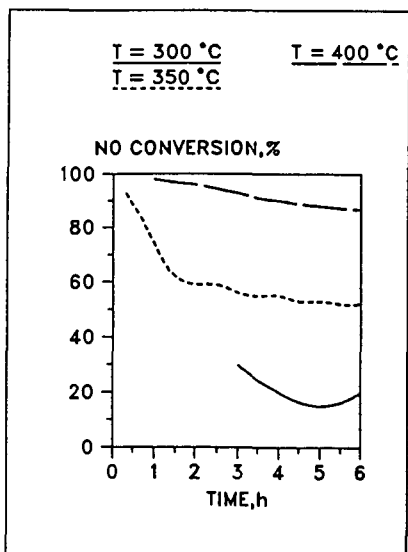
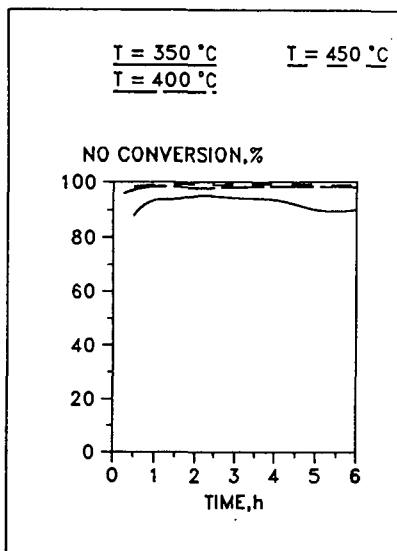


Figure 8. The influence of  $\text{SO}_2$  on the NO conversion with the  $\text{Cr}/\text{Al}_2\text{O}_3$  catalyst ( $\text{NO}=500$  ppm,  $\text{NH}_3/\text{NO}=1$ ,  $\text{SV}=3.2 \text{ s}^{-1}$ ,  $\text{SO}_2=500$  ppm).

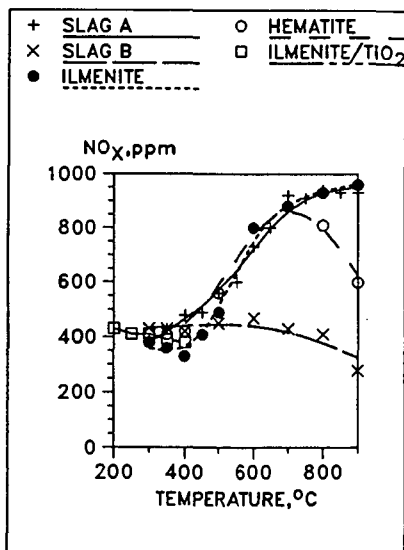


Figure 9. NO conversion with the other catalysts ( $\text{NO}=500$  ppm,  $\text{NH}_3/\text{NO}=1$ ,  $\text{SV}=3.6 \text{ s}^{-1}$ ,  $\text{SO}_2=0$ ).

Figure 10. The influence of the  $O_2$  concentration on the NO conversion with the  $V/TiO_2$  catalyst ( $NO=500$  ppm,  $NH_3/NO=1$ ,  $SV=3.4-3.6$  s $^{-1}$ ,  $SO_2=0$  ).

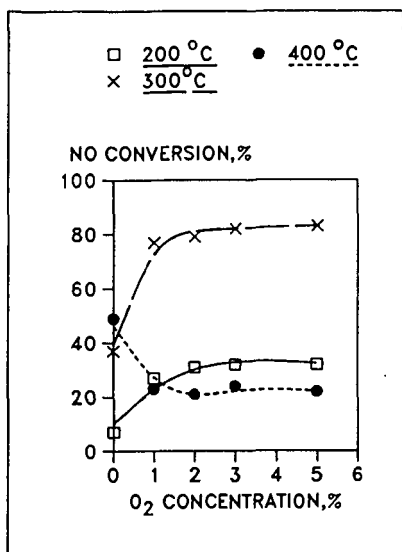


Figure 11. The influence of the  $O_2$  concentration on the NO conversion with the  $Cu/TiO_2$  catalyst ( $NO=500$  ppm,  $NH_3/NO=1$ ,  $SV=3.4-3.6$  s $^{-1}$ ,  $SO_2=0$  ).

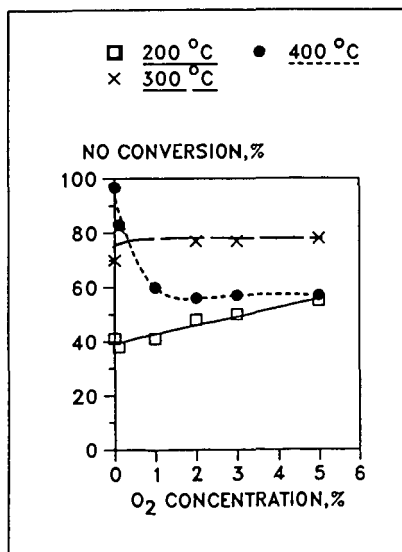
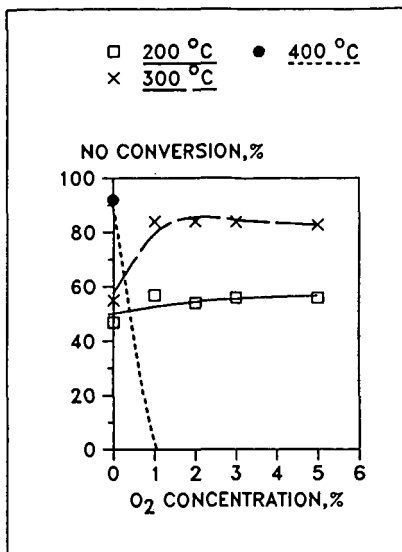


Figure 12. The influence of the  $O_2$  concentration on the NO conversion with the  $Cu/Al_2O_3$  catalyst ( $NO=500$  ppm,  $NH_3/NO=1$ ,  $SV=3.4-3.6$  s $^{-1}$ ,  $SO_2=0$  ).

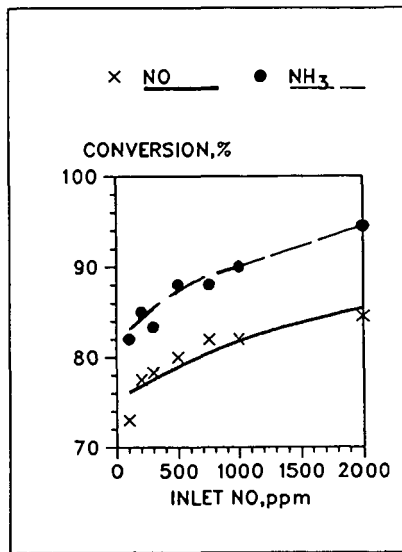


Figure 13. The influence of the NO inlet concentration on the NO conversion with the  $Cu/Al_2O_3$  catalyst ( $NH_3/NO=1$ ,  $O_2=5$  %,  $SV=3.6$  s $^{-1}$ ,  $SO_2=0$  ).